

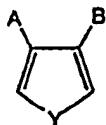
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(54) Polymerizable pyrroles and thiophenes

(57) Compounds represented by the following formula:

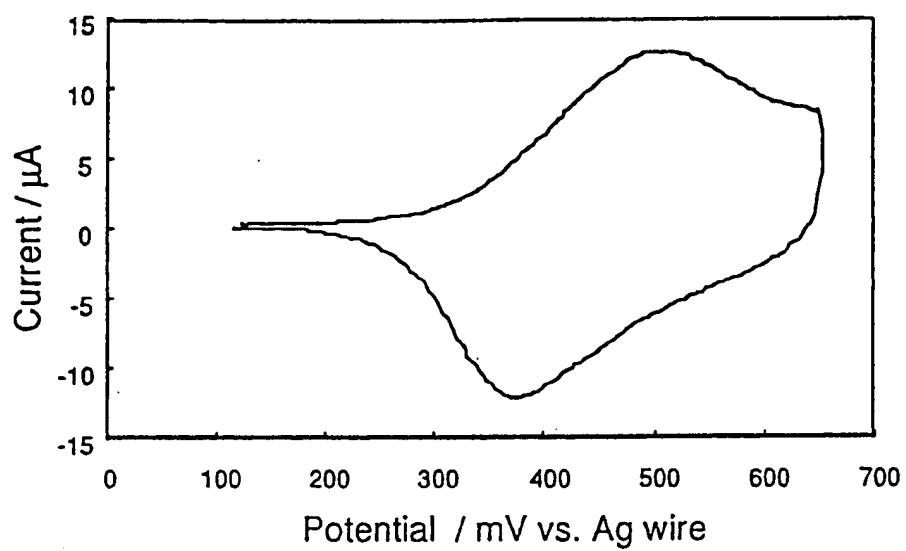


wherein Y represents NH or S; A represents hydrogen, a halogen atom or $-(CH_2)_m-SR^1$; and B represents $-(CH_2)_n-SR^2$, $-R^3-(S)_p-R^4$ - - R^5-SR^6 , $-(S)_q$ - or $-SR^7$,

where R^1 , R^2 , R^6 and R^7 each represent hydrogen, an alkyl group, an alkylcarbonyl group or an aryl group; R^3 , R^4 and R^5 each represent an alkylene group or an arylene group; m and n each independently represent an integer of 0, 1, 2 or 3, provided that m and n are not 0 simultaneously; p and q each independently represent an integer of 0, 1 or 2; and Y' represents NH or S; and A and B may be combined to form $-(CH_2)_m-S-S-(CH_2)_n-$, may be used for preparing electroconductive polymers and electrode active substances.

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Fig. 1



Novel Sulfur-Containing Compound and Method for Preparation of The Same

This invention relates to novel sulfur-containing compounds, a method for preparation of the same, an electroconductive polymer derived therefrom, a method for preparation of the same, and an electro active substance comprising the same. More specifically, this invention relates to novel sulfur-containing compounds which are available as intermediates for pharmaceutical and agrochemical active ingredients, oil/water additive, vulcanizer for a rubber or an industrial biocide, and a method for preparation of the same.

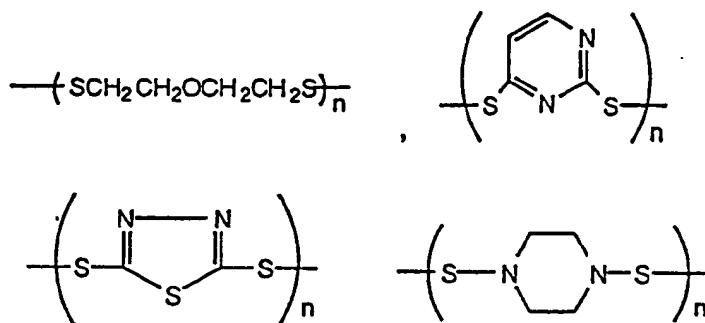
There are many publications treating the miniaturization of batteries and for such purposes, conductive polymers are drawing attention as new electro active substances. Among others, polypyrrole and polyaniline are promising with their stable redox characteristic and excellent charge-discharge repetition property. Papers treating polypyrrole analogous as an electro active substance are many because pyrrole monomers can readily be modified to provide polymers with various functional properties.

Polypyrrole, however, tends to cause irreversible over oxidation during charging, by giving up one as usual or more electrons from 3 pyrrole monomers. In this point of view, polyaniline is preferred because, for the latter, one electron can be deducted per monomer unit, leading to a higher charge capacity than the former, as described in Japanese Patent Kokai Sho 62- 226568 as for polypyrrole and Japanese Patent Kokai 2-638 as for polyaniline.

Also, Japanese Patent Kokai Hei 4-155766 (28.5.92; Priority 2-280455 JP/ Oct. 18, 90), Hei 4-439020 (26.8.92; Priority 3-11665 JP/ Jan. 9, 91) and Kokai Hei 4-239510 (27.8.92; Priority 3-22611/ Jan. 24, 1991) by Fuji Photo Film Co. propose polypyrrole with improved conductivity as compared with polypyrrole or polythiophene, characterized by providing at the 3- and 4-positions of the repeating unit with carbonyl groups.

Disulfide compounds are also drawing attention recently as alternative electro active substance with a large charge storage capacity. For the practical use of disulfide compounds, they are dispersed in a form of solid particles on substrate or in conducting matrix. In addition, disulfide compounds are insulators and therefore only the surface of the particle is accessible for electron transfer reactions.

The disulfide compounds, as shown below, have been proposed as electro active substances by taking advantage of their redox potentials by S.J. Visco et al. [Mol. Cryst. Liq. Cryst. pp. 185, 1990; J. Electrochem. Soc. Vol. 135 (12), 2905 (1988); ibid., Vol. 136 (3), 661 (1989)]. In addition, polymers derived from disulfide compounds are proposed by Visco et al [J. Elec. Chem. Soc. Vol. 139 (7), 1808 (1992); ibid., Vol. 138 (7), 1896 (1991)].



wherein n represents an integer of 2 or more.

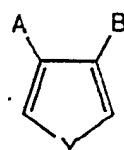
The proposed polymers by Visco et al. consist of -S-S- bonds in the polymer main chain for the repeating unit for polymers, as shown in above.

Cyclic disulfide compounds and polymers thereof are also proposed as a conductive polymer material in Japanese patent Kokai Hei 4-155766 (28.5.92; Priority Hei 2-280455 JP/ 18.10.90).

The present invention is a new concept in linking disulfide groups to a potentially conducting polymer systems and improve this way the accessibility to additional charge storage sites.

The present invention relates to novel sulfur-containing compounds, a method for preparation of the same, an electroconductive polymer derived therefrom, a method for preparation of the same, and an electro active substance comprising the same.

The compound of the present invention is represented by the following formula:

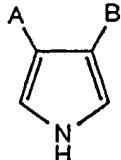


wherein Y represents NH or S; A represents hydrogen, a halogen atom or $-(CH_2)_m-$ SR^1 ; and B represents $-(CH_2)_n-SR^2$, $-R^3-(S)_p-R^4-$  $-R^5-SR^6$, $-(S)_q-$  or $-SR^7$,

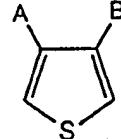
where R^1 , R^2 , R^6 and R^7 each represent hydrogen, an alkyl group, an alkylcarbonyl group or an aryl group; R^3 , R^4 and R^5 each represent an alkylene group or an arylene group; m and n each independently represent an integer of 0, 1, 2 or 3, provided that m and n are not 0 simultaneously; p and q each independently represent an integer of 0, 1 or 2; and Y' represents NH or S; and A and B may be combined to form $-(CH_2)_m-S-S-(CH_2)_n-$.

More specifically, the compounds of invention are represented by the general formulae [1] and [2] mentioned below:

[1]



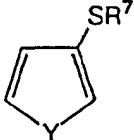
[2]



wherein A and B each have the same meanings as defined above.

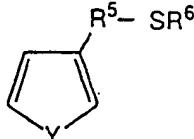
More concrete examples of the compounds of the present invention are represented by the formulae [3] - [9]:

[3]



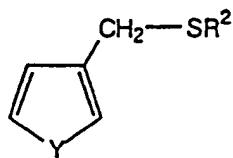
wherein R^7 represents hydrogen, an alkyl group, an alkylcarbonyl group or an aryl group; and Y represents an imino group or sulfur atom;

[4]



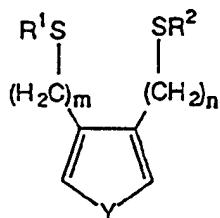
wherein R^5 represents an alkylene group or an arylene group; R^6 represents hydrogen, an alkyl group or an aryl group; and Y represents an imino group or sulfur;

[5]



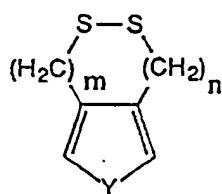
wherein Y represents an imino group or sulfur; and R^2 represents hydrogen, an alkyl group, an alkylcarbonyl group or an aryl group;

[6]



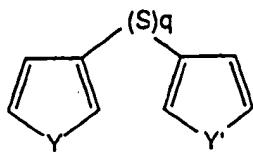
wherein Y represents an imino group or sulfur; R^1 and R^2 each represent hydrogen, an alkyl group, an alkylcarbonyl group or an aryl group; and m and n each represent an integer of 0, 1, 2 or 3 provided that m and n are not 0, simultaneously;

[7]



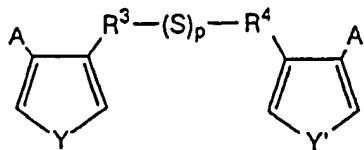
wherein Y represents an imino group or sulfur; and m and n each represent an integer of 0, 1, 2 or 3 provided that m and n are not 0, simultaneously;

[8]



wherein Y and Y' each represent an imino group or sulfur; and q represents an integer of 1 or 2; and

[9]



wherein A represents hydrogen or a halogen atom; Y and Y' each represent an imino group or sulfur; R³ and R⁴ each represent an alkylene group or an arylene group; and p represents an integer of 1 or 2.

Fig. 1 shows a curve of the current (μ A) vs. potential (mV) of a polymer obtained in Example 10.

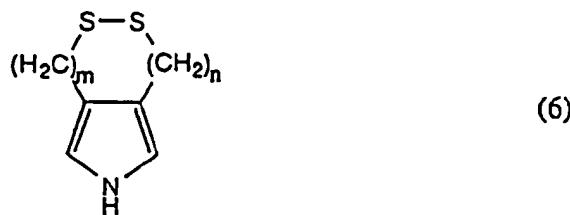
The present invention will be described in detail below.

An alkyl group is preferably those having 1 to 6 carbon atoms, more preferably 1 to 3 carbon atoms such as methyl, ethyl and propyl. An alkylcarbonyl group is preferably those having 2 to 7 carbon atoms, more preferably 2 to 4 carbon atoms, particularly preferably acetyl. An aryl group is preferably phenyl or naphthyl which may be substituted, more preferably phenyl.

An alkylene group is preferably those having 1 to 6 carbon atoms, more preferably 1 to 3 carbon atoms such as methylene, ethylene and propylene. An arylene group is preferably a phenylene group or a naphthylene group, more preferably a phenylene group.

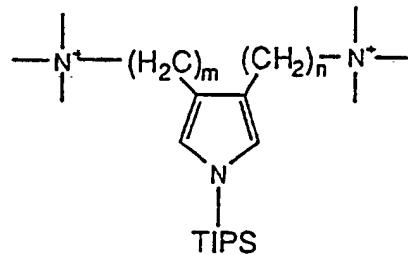
The sulfur-containing compound of the present invention can be synthesized by starting from N-triisopropyl silyl-pyrrole or 3,4 -dimethyl thiophene generally explained as follows:

a) Method for preparation of the compound represented by the following formula (6):



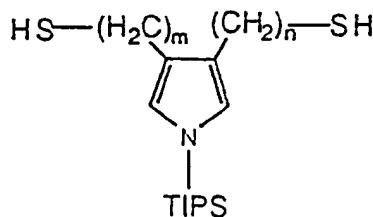
wherein m and n each represent an integer of 0, 1, 2 or 3, provided that m and n are not 0, simultaneously,

can be carried out by reacting a starting compound represented by the following formula:



wherein TIPS represents triisopropylsilyl, and m and n have the same meanings as defined above,

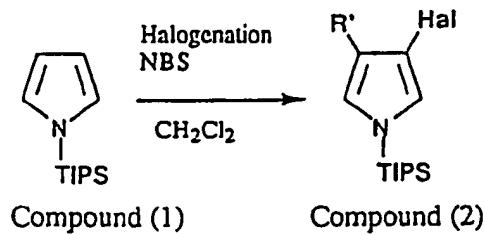
with a thiolating agent such as NaSH in an organic solvent such as dimethylformamide (DMF) at a temperature of below 0 °C to room temperature for 0.5 to 5 hours to obtain a compound represented by the following formula:



wherein m and n have the same meanings as defined above, followed by conversion of said compound to the objective compound of the above formula (6) in the presence of Ellman's reagent in an aqueous organic solvent such as methanol, ethanol and so on at a temperature of below 0 °C to room temperature for 0.5 to 5 hours.

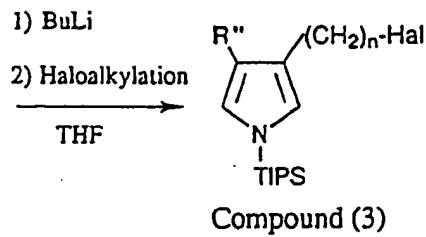
b) Method for preparation of the compound represented by the above formula (6) can be also effected by conducting the reactions in the following Schemes (1) - (5):

Scheme (1)



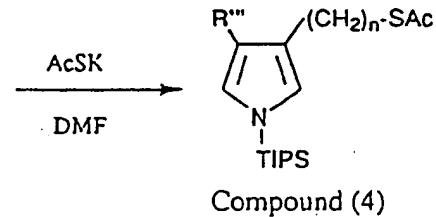
wherein TIPS represents triisopropylsilyl; R' represent hydrogen or a halogen atom; and Hal represents a halogen atom.

Scheme (2)



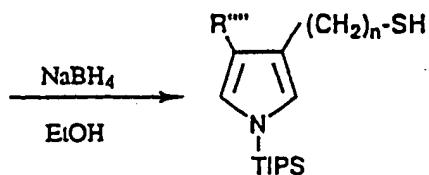
wherein R'' represents a halogen atom or $-(\text{CH}_2)_m\text{-Hal}$; and m and n each represent an integer of 0, 1, 2 or 3, provided that m and n are not 0, simultaneously.

Scheme (3)



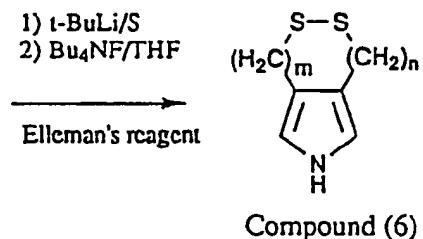
wherein R''' represents a halogen atom or $-(\text{CH}_2)_m\text{-SAC}$; and Ac represents acetyl.

Scheme (4)



Compound (5)
wherein R''' represents a halogen atom or $-(\text{CH}_2)_m\text{-SH}$.

Scheme (5)



Compound (6)

Namely, the reaction of Scheme (1) is carried out by subjecting the starting compound (1) to halogenation reaction in the presence of a halogenating agent such as N-bromo-succinimide (NBS) in an organic solvent such as tetrahydrofuran (THF), dichloromethane and so on in an inert atmosphere such as N_2 , Ar, etc., at a temperature below 0 °C to obtain a halogenated compound (2).

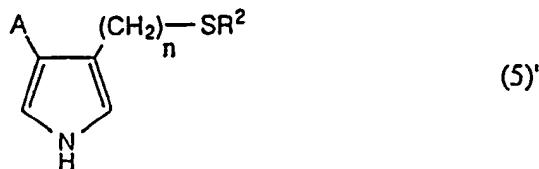
The reaction of Scheme (2) is carried out by reacting a haloalkylation agent such as 1,3-dibromopropane in the presence of a catalyst such as butyl lithium in an organic solvent such as THF, dimethoxyethane (DME), ether, dichloromethane and so on in an inert atmosphere such as N_2 , Ar, etc., at a temperature below 0 °C to obtain a haloalkylated compound (3).

The reaction of Scheme (3) is carried out by using a thiolating agent such as potassium thioacetate in an organic solvent such as THF, DMF, dichloromethane and so on in an inert atmosphere such as N_2 , Ar, etc., at a temperature of below 0 °C to room temperature to obtain a thiolated compound (4).

The reaction of Scheme (4) is carried out by reducing the resulting compound (4) in the presence of a reducing agent such as sodium borohydride in an organic solvent such as ethanol and so on in an inert atmosphere such as N_2 , Ar, etc., at a temperature of below 0 °C to room temperature to obtain a thiol compound (5).

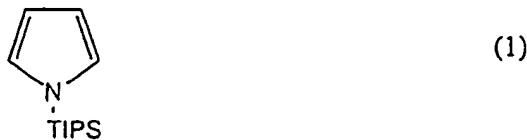
The reaction of Scheme (5) is carried out by using a dithiol compound as a starting material to cyclize the dithiol portion. That is, the dithiol compound is treated by tert-butyl lithium and sulfur powder in an organic solvent such as THF, DME and so on in an inert atmosphere such as N₂, Ar, etc., at a temperature below 0 °C and then treated by Bu₄NF in an organic solvent such as methanol, ethanol and so on at the same temperature. Then, the thus treated compound is treated with the Ellman's reagent at a pH of about 7 at a temperature of below 0 °C to room temperature for 0.2 to 5 hours to obtain the desired compound (6).

c) Method for preparation of the compound represented by the general formula (5)':



wherein A represents hydrogen or -(CH₂)_m-SR¹; R¹ and R² each represent hydrogen, an alkyl group or an aryl group; and m and n each represent an integer of 0, 1, 2 or 3,

can be carried out by halogenating the starting compound represented by the following formula (1):



wherein TIPS has the same meaning as above,

by the method, for example, as described in T.T. Tidwell et al., *J. Org. Chem.*, 55, 6317 (1990) to obtain an intermediate represented by the following formula (2):



where R' represents hydrogen or a halogen atom, and Hal has the same meaning as above,

followed by lithiation and haloalkylation in the same manner as mentioned in the above Scheme (2) to obtain the compound represented by the following formula (3):



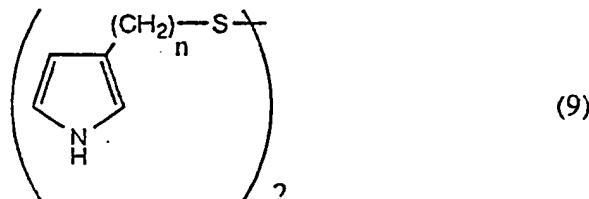
wherein R'' represents hydrogen or $-(CH_2)_n$ -halogen,
then converting (3) by thiolation in the same manner as mentioned in the above Scheme
(3) to the thioester represented by the following formula (4):



wherein Ac represents acetyl group; and R''' represents hydrogen or $-(CH_2)_n$ -
SAc,

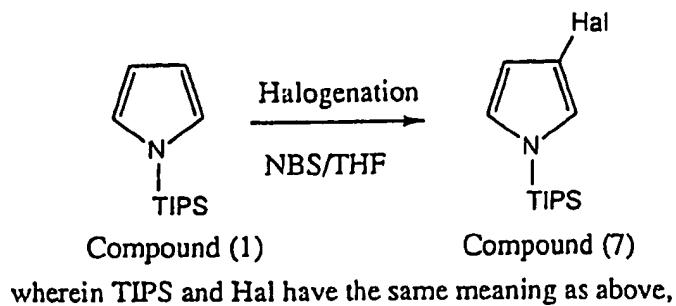
and finally reducing (4) in the same manner as mentioned in the above Scheme (4) and
deprotecting the reduced compound in a conventionally known manner to form the
sulfur-containing pyrrole derivatives (5)'.

d) Method for preparation of the compound represented by the following formula (9):

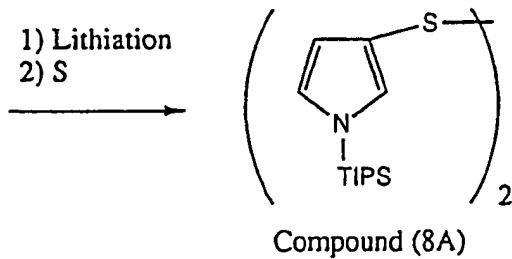


wherein n represents an integer of 0, 1, 2 or 3,
can be carried out by halogenating compound (1) to obtain intermediate (7), lithiation of
(7), followed by reaction with sulfur to give (8A) or by alkylation, reaction with
NaSH, conversion to disulfide (8B), and finally deprotection of (8A) and (8B) to form
Compound (9), as mentioned by the following Schemes (6), (7A), (7B) and (8):

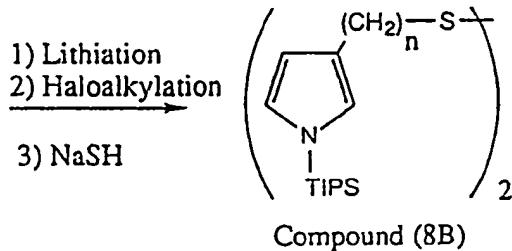
Scheme (6)



Scheme (7A)

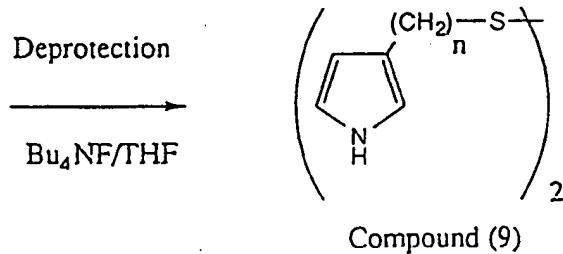


Scheme (7B)



wherein n represents 1, 2 or 3,

Scheme (8)



wherein n represents 1, 2 or 3.

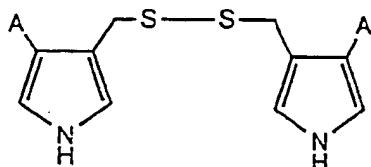
Namely, the reaction of Scheme (6) can be carried out by subjecting the TIPS-protected pyrrol to halogenation reaction in the same manner as in Scheme (1) as mentioned above to obtain Compound (7).

The reaction of Scheme (7A) can be carried out by subjecting the resulting Compound (7) to lithiation in the presence of butyl lithium with sulfur powder in an organic solvent such as THF, DME and so on at a temperature of below 0 °C to room temperature in an innert atmosphere for 0.5 to 5 hours to obtain Compound (8A).

The reaction of Scheme (7B) can be carried out by subjecting the resulting Compound (8A) to lithiation in the same manner as in Scheme (7A) and then subjecting to haloalkylation in the same manner as in Scheme (2) as mentioned above to obtain Compound (8B).

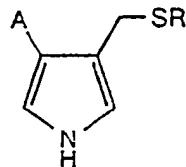
Then, the resulting compound (8B) is subjected to deprotection in the presence of Bu₄NF in an organic solvent such as THF, DMF and so on at a temperature of below 0 °C to room temperature for 0.2 to 5 hours to obtain Compound (9).

e) Method for preparation of the compound represented by the following formula :



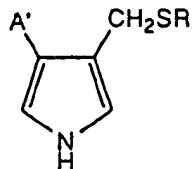
wherein A represents hydrogen, an alkyl group, an alkylcarboxyl group or an aryl group,

can be carried out by using Ellmann's reagent to convert a thiol intermediate represented by the following formula:



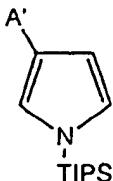
wherein A and R have the same meanings as defined above, to the objective disulfide compound. The reaction conditions are substantially the same as the latter reaction of Scheme (5).

f) Method for preparation of the compound represented by the following formula:



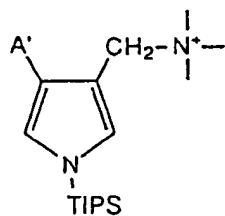
wherein A' represents hydrogen, SR¹ or -(CH₂)_m-SR²; and R represents hydrogen, an alkyl group or an aryl group,

can be carried out by reacting a starting compound represented by the following formula:



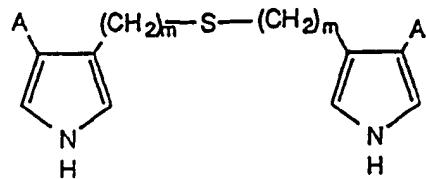
wherein A' and TIPS have the same meanings as above,

with the Eschenmoser's salt, CH₂=N⁺(CH₃)₂I⁻ at a temperature of an ambient temperature in an organic solvent such as THF, DMF, methyl cyanide (CH₃CN) and so on under an inert gas stream such as N₂, Ar and so on for 0.2 to 10 hours, and then with methyl iodide (MeI) at a temperature below 0 °C to room temperature in an organic solvent such as THF, ether and so on under an inert gas stream such as N₂, Ar and so on for 0.2 to 10 hours to give an intermediate represented by the following formula:



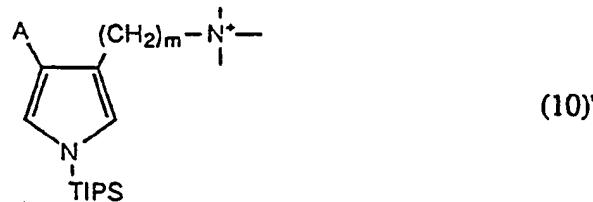
and reacting the resulting salt with Na SR or KSR where R has the same meaning as defined above in an organic solvent such as THF, DMF and so on at a temperature below 0 °C under an inert atmosphere such as N₂, Ar and so on for 0.2 to 10 hours to obtain the above objective compound.

g) Method for preparation of the compound represented by the following formula:



wherein A represents hydrogen, a halogen atom or $-(CH_2)_m-SR^1$, and m represents an integer of 1, 2 or 3,

can be carried out by converting an intermediate (10)' represented by the following formula:



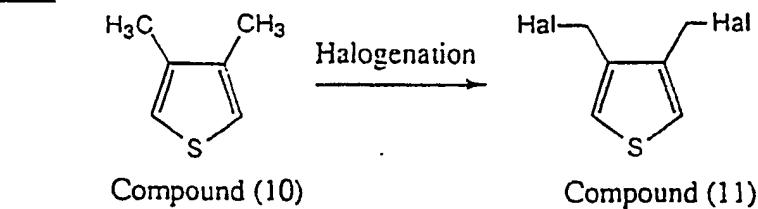
wherein A and TIPS have the same meanings as defined above, in the presence of an alkali metal sulfide such as Na_2S in an organic solvent such as DMF at a temperature of below 0 °C to room temperature under an inert atmosphere such as N_2 , Ar and so on for 0.2 to 10 hours to obtain the above objective compound.

h) Method for preparation of the compound represented by the following formula (14):



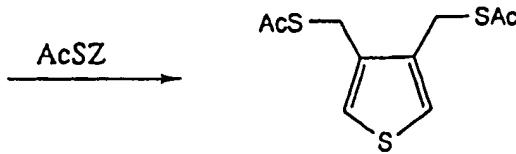
characterized by conducting the reaction in accordance with the following Schemes (9), (10), (11) and (12):

Scheme (9)



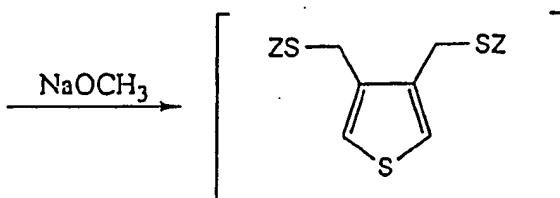
wherein Hal represents a halogen atom,

Scheme (10)



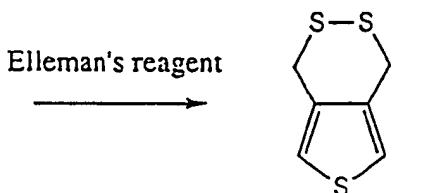
wherein Ac represents an acetyl group; and Z represents an alkali metal,

Scheme (11)



wherein Z has the same meaning as defined above,

Scheme (12)



Compound (14)

Namely, in the reaction of Scheme (9), the starting compound (10) is halogenated by using a halogenating agent such as NBS (N-bromosuccinimide) in the presence of AIBN (azobisisobutyronitrile) in an organic solvent such as benzene, THF and so on at a temperature of the boiling point of a solvent to be used or lower under an inert atmosphere such as N₂, Ar and so on for 0.1 to 10 hours to obtain Compound (11).

In the reaction of Scheme (10), Compound (11) is subjected to thioesterification by using an alkali metal thioacetate such as potassium thioacetate represented by the following formula:



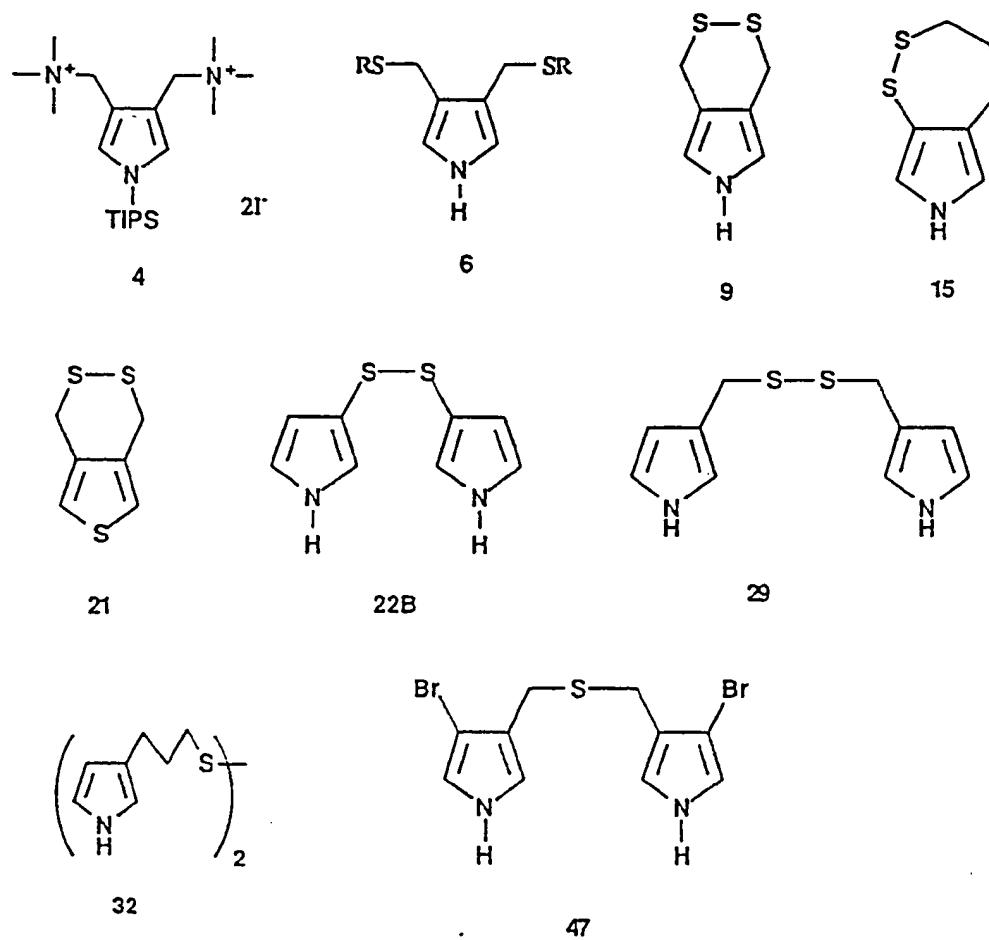
wherein Ac and Z have the same meanings as defined above,
at a temperature of room temperature or lower in a solvent such as DMF, THF and so on under an inert atmosphere such as N₂, Ar and so on for 0.1 to 10 hours to obtain

Compound (12).

In the reaction of Scheme (11), Compound (12) is subjected to deacylation by hydrolysis or reduction using, for example, an alkali metal alkoxide such as sodium methoxide in an alcoholic solvent such as methanol, ethanol and so on at a temperature of room temperature or lower under an inert atmosphere such as N_2 , Ar and so on for 0.1 to 10 hours to obtain Compound (13).

In the reaction of Scheme (12), Compound (13) is converted by using Ellman's reagent under substantially the same reaction conditions as in Scheme (5) mentioned above to obtain the objective disulfide compound (14).

In the compounds of the present invention, preferred are as follows:



Among them, particularly preferred are 3,4-bis(1H-pyrrolyl)methyl-1H-pyrrole

(Compound 6a); ethanecarbothioic acid .S-(4-acetylsulfanyl)methyl-1H-pyrrol-3-ylmethyl) ester (Compound 6b); 3,4-bis-ethylsulfanyl)methyl-1H-pyrrole (Compound 6c); 2,7-dihydro-4H-5,6-dithia-2-aza-indene (Compound 9); 2,6,7,8-tetrahydro-4,5-dithia-2-aza-azulene (Compound 15); 1H,4H-thieno[3,4-d][1,2]dithiine (Compound 21); and bis(pyrrole)disulfide (Compound 22B).

Thus prepared compounds of the present invention are per se promising as pharmaceutical and agrochemical intermediates, oil/water additives, vulcanizers for rubber, industrial biocides, etc.

Moreover, the compounds are susceptible to polymerization in chemical and electrochemical manners to provide electrically conductive substances.

The method of polymerization can be selected from electrochemical manner and chemical manner depending on the structure of the monomers and cost. The compounds represented by the general formulae [1] and [2], and optional mixtures thereof can be polymerized on an electrode surfaces in organic solvents in the presence of supporting electrolytes, provided that R¹, R^{1'}, R², R³, R⁴, R⁵, R⁶ and R⁷ are not aryl. Some examples for solvents are, but not limited to, organic solvents such as acetonitrile, DMF (dimethylformamide), dimethyl acetamide, DMSO (dimethylsulfoxide), formamide, dimethoxyethane, nitromethane, propylene carbonate, etc. or mixtures thereof. The supporting electrolytes are, for example but not limited to, salts of alkali metal cations such as Li⁺, Na⁺, and anions such as BF₄⁻, AsF₆⁻, PF₆⁻, ClO₄⁻, HSO₄⁻, etc. and polyanions such as sulfated or sulfonated thermoplastic polymers. Preferred anode materials are, for example, metal electrodes such as Ti, Ni, Pt, Steel, etc. or ITO glass, and polymerization can be conducted at a current density of 0.5 - 20 mA/cm², or more preferably 1 - 5 mA/cm². The products on the electrode surfaces can be readily peeled off and purified by washing.

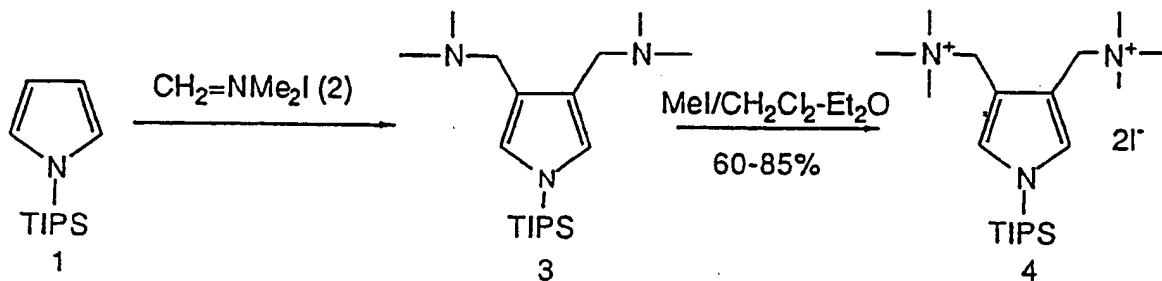
Chemical oxidative polymerization can be achieved in solvents mentioned before and water in the presence of oxidizing agents composed of chloride, more generally halide and other oxidation stable anion (BF₄⁻, PF₆⁻, etc.) salts of Fe³⁺, Al³⁺, Ru³⁺, Pt⁴⁺, Pd⁴⁺, etc., and peroxides such as H₂O₂, K₂S₂O₈, etc. and organic oxidants, tetrachlorobenzoquinone and the like.

The polymer materials thus prepared can be used as antistatic ingredients for polymer films, capacitors, sheet type heating elements. Especially, the polymer is promising as

an electro active substance for battery uses because of its high redox efficiency per unit weight.

The following examples are presented for the purpose of illustration only and are not to be construed to limit the nature and scope of the present invention in any manner whatsoever.

Example 1: Preparation of Pyrrole Intermediate 4



wherein TIPS represents $(\text{iso-propyl})_3\text{Si}$.

a) Alkylation at the 3,4-positions

The alkylation at the 3,4-positions is preferably carried out in the manner as described in ETH Thesis (1986) by Dr. Th. Früh, and in *Helv. Chim. Acta.* 70, 1115 (1987) by A. Eschenmoser et al.

N-Triisopropylsilylpyrrole 1 (1-TIPS-Pyrrole, 22.3 g, 0.1 mole) was dissolved in dried acetonitrile (150 ml). Then the Eschenmoser's salt (2, 38.8 g, 0.21 mole) was added at room temperature, while stirring under N_2 . The reaction was carried out at room temperature for 30 min, 60 °C for 1 hour, refluxing for 3.5 hours. Then it cooled to room temperature and the solvent was evaporated. The reaction mixture was redissolved in CH_2Cl_2 (300 ml) and cooled with ice-bath. Cooled 1N NaOH (150 ml) was added, stirring till the color changed to a light yellow. Then the organic phase was collected and washed with additional cold 1N NaOH (150 ml) quickly, then with water and dried over K_2CO_3 . Evaporation of the solvent gave the expected 3,4-dimethylaminomethyl-1-TIPS-pyrrole 3 (32 g, crude yield: 95 %).

b) Methylation with methyl iodide

The above obtained pyrrole 3 (6 g, 17.8 mmole) was dissolved in CH_2Cl_2 (60 ml) and cooled with an ice-bath. A solution of methyl iodide (3.6 ml) in ether (50 ml) was added within 20 min and the reaction was finished after about 10 hours stirring. The

colorless solid salt was filtrated and washed with ether and dried. A colorless powder 4 was obtained (10.2 g, 92 %).

Physical properties of pyrrole 3 and the colorless powder 4 are as follows.

3: Yellowish liquid

NMR (CDCl_3 , 90 MHz): δ 6.684 (s, 2H), 3.413 (s, 4H), 2.286 (s, 12H), 1.11-1.7 (m, 21H).

4: Colorless powder

NMR (DMSO-d_6 , 90 MHz): δ 7.3 (s, 2H), 4.46 (s, 4H), 3.0 (s, 18H), 1.0-1.8 (m, 21H).

Example 2: Substitution reaction of 4 with Alcohol or Thiols



wherein R represents phenyl, acetyl and ethyl in 6a, 6b and 6c, respectively.; and TIPS has the same meaning as above.

The corresponding thiol was dissolved in DMF and stirred with ice cooling. Then an equivalent 1N KOH solution was added to generate the thiolate. After stirring for about 10 min, the solution of pyrrole salt 4 in DMF was added. Nitrogen was introduced in order to remove the trimethylamine from the reaction. The reaction mixture was extracted with ethyl acetate or ether and column chromatographed on silica gel column. Compounds 6 could be obtained in moderate yield.

Physical properties of the resulting compounds 6 are as follows.

6a: Colored oil, yield: 85 %

MS, m/e: 311 (M^+), 202

NMR (CDCl_3 , 90 MHz): δ 7.95 (br, 1H), 7.1-7.5 (m, 10H), 6.62 (d,

$J=2.64\text{Hz}$, 2H), 4.13 (s, 4H)..

UV (EtOH), λ_{max} (ϵ) nm, 208 (2.2×10^4), 255.5 (1.44×10^4).

6b: Oil, yield: 30 %

MS, m/e: 242 (M⁺), IR: 3400, 1680 (cm⁻¹)

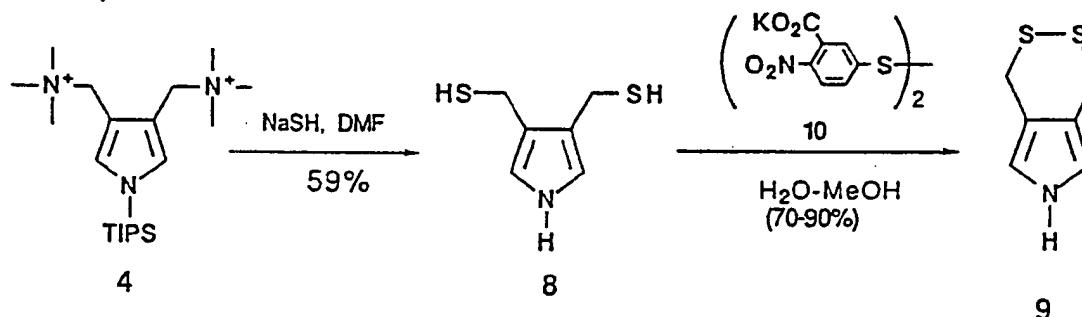
NMR (CDCl₃, 90 MHz): δ 8.0 (br, 1H), 6.697 (d, J=2.64Hz, 2H), 4.032 (s, 4H), 2.328 (s, 6H).

UV (EtOH), λ_{max} (e) nm, 205.5 (1.24x10⁴), 231.5 (1.28x10⁴).

6c: Colorless liquid, yield: 60 %

NMR (CDCl₃, 90 MHz): δ 8.0 (br, 1H), 6.642 (d, J=2.64Hz, 2H), 3.375 (s, 4H), 2.489 (q, J=7.47Hz, 4H), 1.245 (t, J=7.47Hz, 6H).

Example 3: Reaction with NaSH, ring closure to the disulfide 9



a) Synthesis of the dithiol 8

Sodium hydrogensulfide hydrate (NaSH·nH₂O, 70 %, 94 mmole, 7.5 g), was suspended in DMF (200 ml) at room temperature with nitrogen bubbling. Then a solution of the pyrrole salt 4 (23.5 mmole, 14.6 g) in DMF (120 ml) was added during 10 min while stirring. After stirring at room temperature for 1 hour, the reaction mixture was extracted with ethyl acetate, dried over anhydrous sodium sulfate. Column chromatography of the resulting mixture on silica gel with CH₂Cl₂ as the eluent gave a liquid product (8, 2.2 g, 59 %).

b) Conversion of 8 to the disulfide 9

Ellman's reagent (10, 2.5 mmole, 1.0 g), as described in W.J. Lee, *J. Org. Chem.*, 56, 7328(1991) was suspended in H₂O (100 ml) and MeOH (5 ml). The pH of the mixture was adjusted to about 7 with saturated NaHCO₃ at room temperature with stirring. Then this solution was cooled with ice-water and a solution of the dithiol 8 (1.6 mmole, 255 mg) in MeOH (10 ml) was added within 5 min. After further stirring at room temperature for 30 min, the reaction mixture was extracted with ethyl acetate. Column chromatography on silica gel (hexane/CH₂Cl₂ = 1:1) gave the expected

disulfide 9 (176 mg, 70 %).

Physical properties of the thiol 8 and the disulfide 9 are as follows.

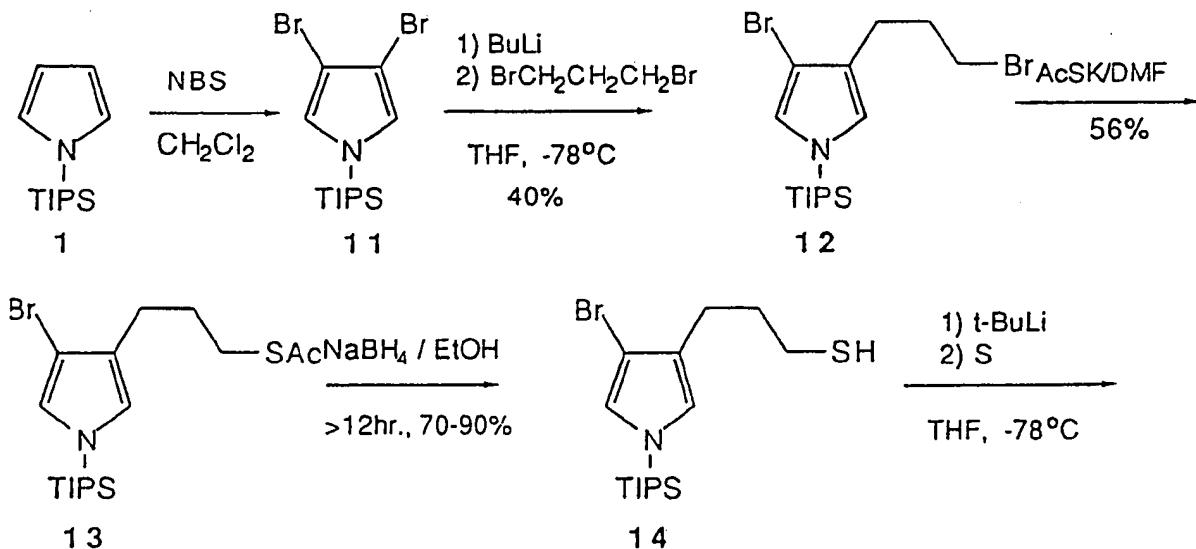
8: Oil

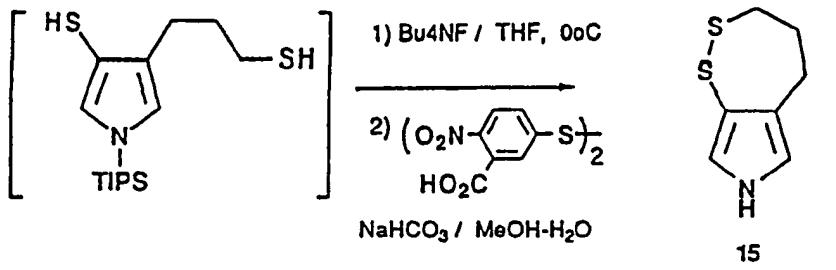
MS (m/e): 159 (M^+), 125, 93, 80 (base peak);
NMR ($CDCl_3$): δ 8.0 (br, 1H), 6.694 (d, $J=2.64$ Hz, 2H), 3.745 (d, $J=6.81$ Hz, 4H), 1.827 (t, $J=6.81$ Hz, 2H).
UV: λ_{max} (e), 206 nm (1.24×10^4),
IR (neat): 3400, 2930, 2550, 1430, 1082 (cm^{-1})

9: Colorless solid

MS (m/e): 157 (M^+), 93;
m.p. 95.5 °C
NMR ($CDCl_3$): δ 7.97 (br, 1H), 6.597 (d, $J=2.64$ Hz, 2H), 3.909 (s, 4H)
IR (KBr): 1430, 1215, 1070, 800 (cm^{-1})
UV: λ_{max} (e), 206.5 nm (0.958×10^4)
Elemental Analysis: C H N
Calc. 45.83 4.49 8.91 (%)
Found 45.97 4.33 8.50

Example 4: 7-membered pyrrole disulfide 15





a) Bromination of 1-TIPS-pyrrole (1)

The bromination was carried out in the manner as described in M. Muchowski, J. Org. Chem., 55, 6317(1990). However, instead of THF (tetrahydrofuran), CH_2Cl_2 which was found to be a good solvent for this dibromination was used. Thus, 1-TIPS-pyrrole (1, 30 mmole, 6.7 g) was dissolved in CH_2Cl_2 (100 ml) and cooled with methanol-dry ice bath to -78°C . Then NBS (N-bromosuccinimide) (20 mmole, 3.56 g) was added with stirring under N_2 . After 10 min, additional NBS (40 mmole, 3.56 x 2) was added (addition of all the NBS in one portion is also possible). Stirring was continued at -78°C for 0.5-1 hour and then the cooling bath was removed. The reaction mixture was allowed to warm up gradually to room temperature, then poured into aqueous NaHCO_3 solution and was extracted with hexane (or dichloromethane). Usual workup gave crude solid product (11.3 g, 98 %). Recrystallization from cold pentane gave pure 3,4-dibromo-1-TIPS-pyrrole(11) as a colorless solid.

b) Lithiation and alkylation with 1,3-dibromopropane

The 3,4-dibromopyrrole 11 (0.762 g, 2 mmole) was dissolved in THF (15 ml) and cooled to -78°C . $\text{BuLi}(1.6\text{M}$ in hexane, 1.4 ml, 2.2 mmole) was added under N_2 . After stirring for 40 min, 1,3-dibromopropane (0.808 g, 4 mmole) was added. Stirring was continued at -78°C for 2.5 hours. Then the cooling bath was removed and the reaction mixture was allowed to warm up to room temperature. Then water was added to quench the reaction. Extraction with ether gave a crude oil. Column chromatography on silica gel eluting with hexane gave the expected product 12 (0.34 g, 40 %) as a colorless liquid.

c) Synthesis of the thio ester 13

Potassium thioacetate (2.28 g, 20 mmole) was suspended in DMF (50 ml) and cooled with ice bath under N_2 . Then a solution of the pyrrole 12 (1.85 g, 4.4 mmole) in DMF (15 ml) was added thereto while stirring for 5 min. The cooling bath was removed after 30 min stirring at 0°C . Extraction with ether gave a mixture of liquid. Column

chromatography on silica gel (hexane/ethyl acetate = 5:1) gave the expected 13 (1 g, 54 %).

d) Reduction to the thiol form 14

Sodium borohydride (0.31 g, 8 mmole) was added to a solution of the starting thioester 13 (1.0 g, 2.08 mmole) in EtOH (50 ml) at 0 °C under N₂. Then the cooling bath was removed and the stirring was continued until the reaction has finished (over 10 hours). The reaction mixture was extracted with ether and Column chromatography on silica gel with hexane/AcOEt (10 : 1) gave liquid product 14 (76-93%).

e) Synthesis of dithiol and conversion to the disulfide 15

Compound 14 (0.3 g, 0.68 mmole) was dissolved in THF (15 ml) and cooled to -78 °C with dry ice-MeOH. t-BuLi (1.5 ml, 2.5 mmole, 1.7 M in pentane) was added under nitrogen. The reaction mixture was stirred for 1 hour at -78 °C. Then sulfur powder (38 mg, 1.2 mmole) was added. The cooling bath was removed after stirring for 1 hour and stirring was continued until it reached room temperature. Then aqueous acetic acid (1 N, 3 ml) was added. The reaction mixture was quickly extracted with ether. An oily product was obtained (200 mg). This crude thiol was redissolved into THF (10 ml) and cooled with ice-water bath under nitrogen. Bu₄NF (2 ml, 1 M in THF) was added. A green solution formed. Then MeOH (5 ml) was added.

The Ellman's reagent 10 (0.4 g) was suspended in MeOH-H₂O (5/50 ml) and the pH of the solution was adjusted to about 7 by use of saturated NaHCO₃. The resulting yellow solution was cooled with an ice-bath. Then the thiolate solution prepared above was added. After stirring at 0 °C for 20 min, the reaction mixture was extracted with ether. Evaporation of the solvent and column chromatography on silica gel with hexane/AcOEt (3 : 1) gave pyrrole disulfide as a colorless solid (15, 30 mg, 25.6 %).

Physical properties of the resulting products are as follows.

12: Colorless oil;

¹H-NMR (CDCl₃): δ 6.70 (m, 1H), 6.53-6.54 (m, 1H), 3.40 (t, J=6.6Hz, 2H), 2.61 (t, J=7.2Hz, 2H), 2.12 (m, 2H), 1.36-1.5 (m, 3H), 1.08 (d, J=7.47Hz, 18H).

13: Colorless oil;

¹H-NMR (CDCl₃): δ 6.68 (d, J=2.4Hz, 1H), 6.49 (d, J=2.4Hz, 1H), 2.89 (t, J=7.1Hz, 2H), 2.52 (t, J=7.47Hz, 2H), 2.33 (s, 3H), 1.83-1.88 (m, 2H), 1.31-1.40 (m, 3H), 1.09 (d, J=7.4Hz, 18H).

14: Colorless oil;

¹H-NMR (CDCl₃): δ 6.69 (d, J=2.4Hz, 1H), 6.48 (d, J=2.4Hz, 1H), 2.51-2.57 (m, 4H), 1.87-1.91 (m, 2H), 1.34-1.44 (m, 4H), 1.08 (d, J=7.47Hz, 18H).

15: Colorless solid;

¹H-NMR(CDCl₃ at 40 °C): δ 7.85 (br, 1H), 6.85-6.87 (m, 1H), 6.59-6.6 (m, 1H), 3.18-3.21 (m, 2H), 2.81-2.84 (m, 2H), 1.95 (br, 2H).

m.p. 87-89 °C;

IR (KBr): 3367, 3112, 1543, 1432, 1398, 1068, 807, 555 (cm⁻¹)

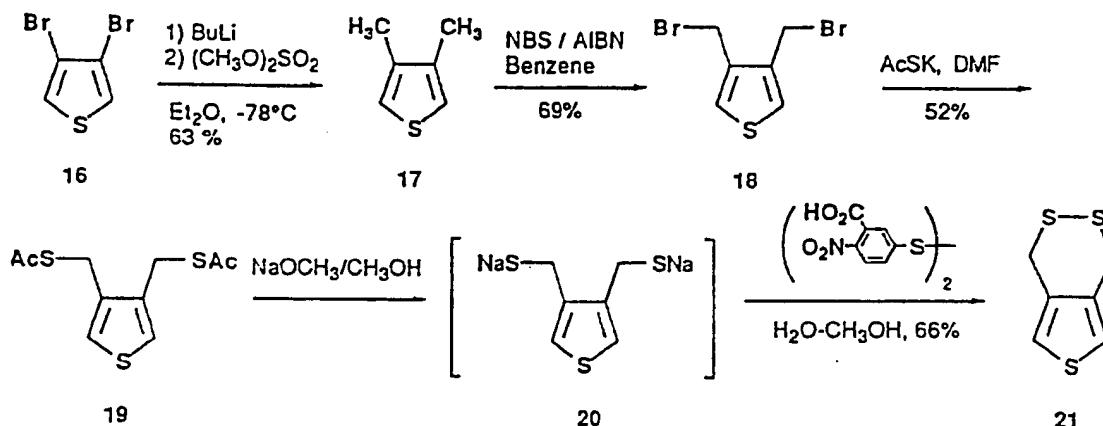
MS: m/e 171 (M⁺).

Elemental Analysis: C H N

Calc. 49.09 5.30 8.18 (%)

Found 49.22 5.19 8.17

Example 5: Synthesis of thiophene-disulfide 21



a) Synthesis of 3,4-dimethylthiophene 17

This compound was synthesized according to a method as described in N. Janda et al., *Synthesis*, 545(1972).

b) Bromination to 18

AIBN (0.33 g, 2 mmole) and 3,4-dimethylthiophene (3.36 g, 30 mmole) were dissolved in benzene (20 ml) and heated to reflux. Then a mixture of NBS (10.7 g, 60 mmole) and AIBN (0.33 g, 2 mmole) was added in portion while maintaining at reflux temperature (10 min). The reaction mixture was then cooled with ice immediately after the addition and was poured into ice-water. Extraction with ether and usual workup

gave a solid product 18 (5.6 g, 69 %). The NMR of this compound is identical with that reported in V.Reinhard Helmers, *J. Prakt. Chem.*, 314(2), 334 (1972).

c) The thio ester 19

Potassium thioacetate (9.12 g, 80 mmole) was dissolved in DMF (60 ml) and cooled with an ice bath. Then a solution of the above made dibromide 18 (5.6 g, 20.7 mmole) in DMF (20 ml) was added in 5 min under nitrogen. The ice bath was removed after the addition and the reaction mixture was stirred at room temperature for 1 hour. Extraction with ether and column chromatography of the resulting oil on silica gel with hexane/AcOEt (10:1 --> 8:1 --> 5:1) gave the expected 19 as an oil (2.8 g, 52 %).

d) Conversion to the disulfide 21

The thioacetate 19 (0.26 g, 1 mmole) was dissolved in MeOH (10 ml) and cooled with ice-bath. Then NaOMe in MeOH (0.6 g, 28 % wt) was added with stirring under nitrogen. This reaction finished in 15 min to give the sodium thiolate 20. This solution was then passed into the ice-cooled solution of the Ellman's reagent (10, 0.6 g, 1.5 mmole) in MeOH-H₂O(5 ml/50 ml) with the pH adjusted to 7 by use of saturated NaHCO₃. Stirring was continued for 30 min. Extraction with AcOEt gave a solid product (0.13 g). Column chromatography on silica gel with hexane/CH₂Cl₂ (10:1) gave the expected disulfide 21 (115 mg, 66 %).

19 : Colorless liquid;

¹H-NMR (CDCl₃): δ 7.186 (s, 2H), 4.09 (s, 4H), 2.35 (s, 6H).

21: Colorless solid; m.p. 92-93 °C;

MS , m/e: 174 (M⁺), 110 (base peak).

¹H-NMR (CDCl₃): δ 7.04 (s, 2H), 4.05 (s, 4H).

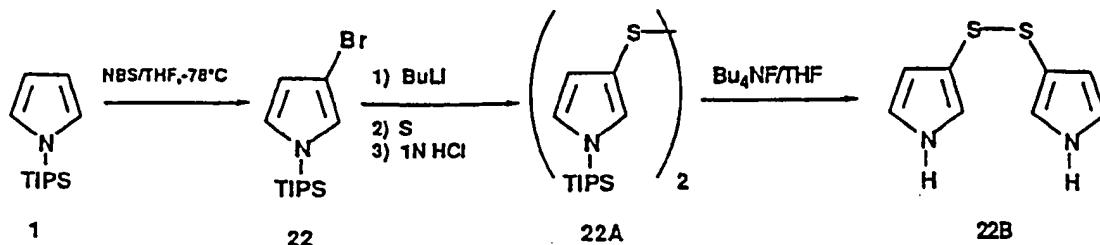
IR (KBr): 3078, 2898, 1363, 1230, 1144, 873, 802 (cm⁻¹)

Elemental Analysis: C H

Calc. 41.35 3.47 (%)

Anal. 41.5 3.04

Example 6: Intramolecular pyrrole disulfide 22B



a) **Bromination of 1**

Bromination of 1-TIPS-pyrrole 1 with NBS to 1-TIPS-3-bromopyrrole 22 was carried out in the manner as described in T.T. Tidwell et al., *J. Org. Chem.*, 55, 6317(1990).

b) **Synthesis of pyrrole disulfide 22B from 22**

The pyrrole 22 (1.51 g, 5 mmole) was dissolved in THF (40 ml) and cooled to -78 °C with dry ice-MeOH bath. t-BuLi (10 mmole, 5.9 ml, 1.9 M in pentane) was added in 5 min under nitrogen. The reaction mixture was stirred at -78 °C for 2 hours. Then sulfur powder (170 mg, 5.3 mmole) was added. The reaction was finished after stirring for 4 hours. The cooling bath was removed and the reaction mixture was allowed to warm-up to room temperature within 1 hour. Then the reaction mixture was poured into ice water and acidified with 1N HCl (5 ml). Extraction with AcOEt gave a liquid product. Column chromatography on silica gel column with hexane/CH₂Cl₂ gave the disulfide 22A (0.5 g, 19.7 %). Deprotection with Bu₄NF (1 M THF solution) in THF at 0 °C gave the expected pyrrole disulfide 22B in 78 % yield.

Physical properties of the resulting product are as follows.

22B: Yellowish solid.

¹H-NMR (CDCl₃): δ 8.3 (br, 2H), 6.89-6.91 (m, 2H), 6.77-6.79 (m, 2H), 6.34-6.36 (m, 2H).

MS, m/e: 196(M⁺), 132, 98(base peak).

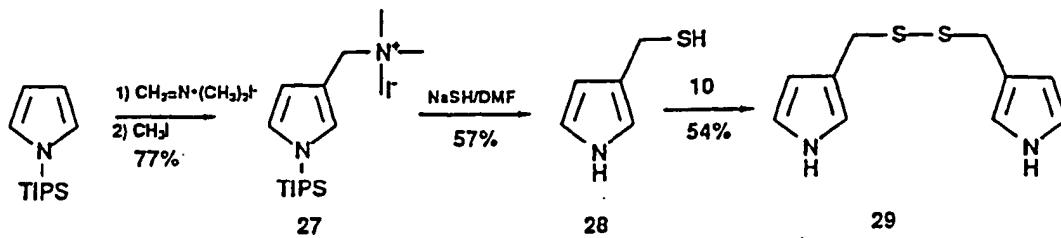
IR(KBr): 3388, 1510, 1400, 1075, 1040, 800 (cm⁻¹)

Elemental Analysis C H N

Calc. 48.95 4.11 14.27 (%)

Found 49.21 3.86 14.02

Example 7: Synthesis of intermolecular disulfide 29



a) Synthesis of pyrrole salt 27

The Eshenmoser's salt (19.4 g, 105 mmole) was added into a solution of 1-TIPS-pyrrole (22.3 g, 100 mmole) in CH_3CN (300 ml) and the reaction mixture was stirred at room temperature under N_2 . After stirring at room temperature for 1 hour, 60 °C for 1 hour, the solvent was evaporated. The reaction mixture was dissolved into CH_2Cl_2 and washed with cold 1N KOH solution. Usual workup gave a crude oil. This oil was again dissolved into ether (300 ml) and cooled with ice. Then a solution of MeI (9 ml) in ether (200 ml) was added in 10 min. The reaction mixture was stirred at 0 °C for 1 hour, then ice bath was removed and stirring was continued for additional 3 hours at room temperature filtration and washing with ether gave colorless solid product 27 (30.5 g, 72 %).

b) Synthesis of thiol 28

Sodium hydrogensulfide ($\text{NaSH}\cdot\text{nH}_2\text{O}$, 70 %, 1.6 g, 20 mmole) was suspended in DMF (50 ml) under N_2 and cooled to -20 °C. Then a solution of pyrrole 27 (4.21 g, 10 mmole) in DMF (40 ml) was added in 30 min with nitrogen bubbling. The reaction mixture was stirred at -20 °C (30 min), room temperature (1.5 hours), and then extracted with AcOEt . A crude liquid (1.2 g) was obtained. Column chromatography on silica gel with CH_2Cl_2 gave the expected thiol 28 (0.64 g, 57 %).

c) Conversion to the disulfide 29

The Ellman's reagent 10 (1.31 g, 3.3 mmole) was suspended in $\text{MeOH-H}_2\text{O}$ (5 ml/100 ml) and cooled with ice bath. The pH of the solution was adjusted to 7 with sat. NaHCO_3 . Then a solution of the thiol 28 (0.45 g, 4 mmole) in MeOH (30 ml) was added in 20 min under N_2 . After stirring for 15 min, the reaction mixture was extracted with AcOEt . Workup gave an oil. Column chromatography on silica gel with CH_2Cl_2 gave the disulfide 29 (0.24 g, 54 %).

Physical properties are as follows.

27: Colorless solid;

NMR(DMSO-d₆), δ 7.1 (s, 1H), 6.94 (m, 1H), 6.4 (m, 1H), 4.35 (s, 2H), 2.95 (s, 9H), 1.3-1.6 (m, 3H), 1.08 (d, J=7.4 Hz, 18H)

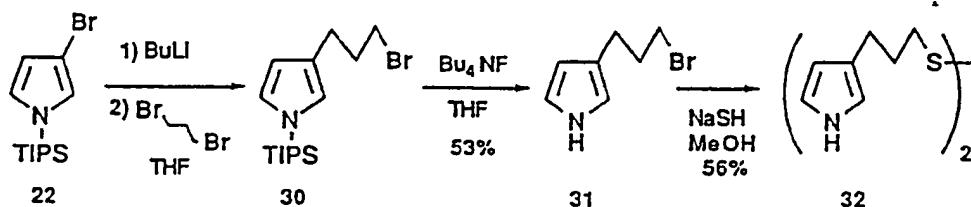
28: Colorless liquid;

¹H NMR (CDCl₃), δ 8.1 (br, 1H), 6.73 (m, 2H), 6.22 (m, 1H), 3.71 (d, J=7.04 Hz, 2H), 1.75 (t, J=7.04 Hz, 1H)
 MS, m/e: 113 (M⁺)

29: Colored solid:

¹H NMR (CDCl₃), δ 8.1 (br, 2H), 6.74 (m, 4H), 6.2 (m, 2H), 3.74 (s, 4H).
 MS, m/e: 224(M⁺), 174

Example 8: Synthesis of pyrrole disulfide 32



a) Alkylation to 31

The 3-bromo-1-TIPS-pyrrole (22, 3.02 g, 10 mmole) was dissolved in THF (50 ml) under N_2 with stirring at -78 °C. BuLi (13 ml, 20.8 mmole, 1.6 M in pentane) was added and the stirring was continued at -78 °C for 4 hours. Then 1,3-dibromopropane (6.06 g, 30 mmole) was added. The reaction mixture was stirred until the bath reached to room temperature (14 hours). Water was added to quench the reaction. Extraction with AcOEt gave a liquid mixture (30 and 1,3-dibromopropane). Deprotection of this product with Bu₄NF in THF at 0 °C gave crude pyrrole 31. Column chromatography on silica gel with CH₂Cl₂ gave 31 as a liquid (1 g, 53 %).

b) Reaction of 31 with NaSH

The starting pyrrole 31 (1.2 g, 6.3 mmole) in MeOH (10 ml) was added to a solution of NaSH·nH₂O (70 %, 1.1 g, 13 mmole) in MeOH (50 ml) at room temperature under N₂. After stirring at room temperature for 30 hours, the reaction mixture was extracted with AcOEt. The resulting crude liquid was purified by column chromatography on silica gel with CH₂Cl₂ to give the expected disulfide 32 (0.5 g, 56 %).

Physical properties are as follows.

31 : Colorless oil;

NMR (CDCl₃): δ 8.0 (br, 1H), 6.5-6.9 (m, 2H), 6.08 (s, 1H), 3.435 (t, J=6.6 Hz, 2H), 2.662 (t, 2H), 1.95-2.3 (m, 2H).

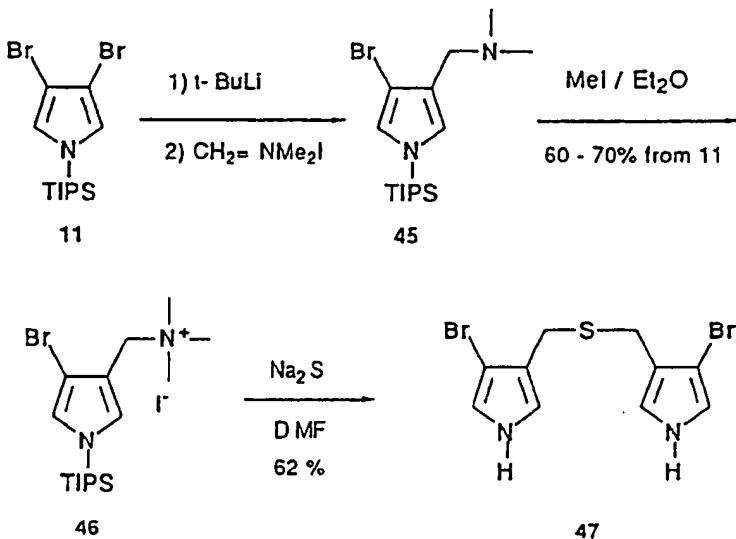
32 : Colorless oil.

NMR(CDCl₃): δ 8.0 (br, 2H), 6.5-6.8 (m, 4H), 6.0-6.2 (m, 2H), 2.4-2.8 (m, 8H), 1.8-2.2 (m, 2H).

MS, m/e: 280 (M⁺), 140, 80 (base peak)

IR(neat): 3405, 2930, 2850, 1431, 1065, 780 (cm⁻¹)

Example 9: Synthesis of Pyrrole-sulfide 47



a) Synthesis of pyrrole 46

The starting 3,4-dibromo-1-TIPS-pyrrole 11 (15.24 g, 40 mmole) was dissolved in THF (200 ml) and cooled to -78 °C under nitrogen. A solution of t-BuLi (49.4 ml, 84 mmole, 1.7M pentane solution) was added while stirring in 15 min. The reaction mixture was stirred at -78 °C for 1 hour. Then the Eschenmoser's salt 2 (7.8 g, 42 mmole) was added in portion. The reaction mixture was stirred overnight while allowing the cooling bath to warm up gradually to room temperature. Extraction with CH₂Cl₂, dried over K₂CO₃ gave crude 45 as a liquid.

The above obtained crude product was dissolved in Et₂O (200 ml) and cooled with ice bath. Then a solution of CH₃I (4 ml, 63 mmole) in Et₂O (50 ml) was added in 30 min. The reaction mixture was stirred overnight and the colorless precipitate was collected ,

washed with Et_2O gave pyrrole mono-salt (46, 14.9 g, 70 %).

b) Reaction of pyrrole mono-salt 46 with Na_2S

The pyrrole mono-salt 46 (1 g, 2 mmole) was dissolved in DMF (15 ml) and cooled to 0 °C under nitrogen. Then $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (1 mmole, 241 mg) was added. After stirring at 0 °C for 5 hours, the reaction mixture was extracted with Et_2O . Workup and column chromatography on silica-gel (hexane / AcOEt = 1:1) gave pyrrole-sulfide 47 as a colorless solid (220 mg, 62 %).

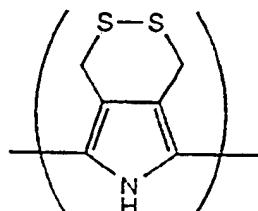
Physical properties are as follows.

46: NMR (CDCl_3): δ 7.34 (d, $J=2.3$ Hz, 1H), 6.83 (d, $J=2.3$ Hz, 1H), 4.68 (s, 2H), 3.38 (s, 9H), 1.56 (m, 3H), 1.1 (d, $J=7.49$ Hz, 18H).

47: NMR(CDCl_3): δ 8.14(br, 1H), 6.7-6.8(m, 4H), 3.58(s, 4H).

Example 10: Chemical polymerization of disulfide 9

Disulfide 9 which was synthesized in Example 3 was chemically polymerized. 2.03 g of ferric chloride dissolved in acetonitrile was dropped onto a 40 ml acetonitrile solution to which 0.365 g (2.5 mmole) of disulfide 9 was dissolved while stirring, and then stirring was continued for 3 hours to obtain black colored precipitates. The precipitates were centrifugally isolated, washed with ion-exchanged water and then dried at 50 °C under vacuum to obtain powdery product. The product is identified with a polymer having the following repeating unit:



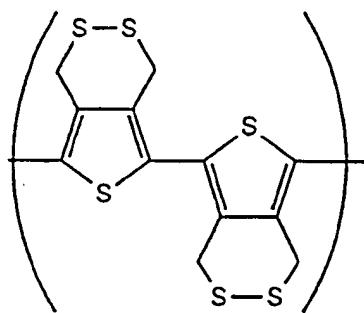
The products are shaped into pellets to determine electro-conductivity by Van der Pauw Method to obtain $7 \times 10^{-5} \text{ S/cm}^{-1}$. This conductivity is much higher than the disulfide compounds proposed by Visco et al. mentioned above.

Also, the electrochemical properties of the product was measured by three electrode cyclic voltammetry in a propylene carbonate solution containing 0.1 M of tetraethyl ammonium, by the use of silver wire as the pseudo reference electrode, and at 100 mV/

s of potential scanning speed. The peaks of the oxidation potential and the reduction potential were respectively 503 mV and 371 mV to the pseudo reference electrode. Fig. 1 shows a curve of the current (μ A) vs. potential (mV).

Example 11: Electro-chemical polymerization of disulfide 21

Disulfide 21 which was synthesized in Example 5 was electrochemically polymerized. 0.02 g of disulfide 21 was dissolved into 10 ml of an acetonitrile solution containing 10 ml of 0.532 g of lithium perchlorate, and electrochemically polymerized by using a platinum disc (area; 0.635 cm²) for working electrode, platinum coil as the counter electrode, and silver - silver chloride as the reference electrode to obtain black colored film of the surfaces of the working electrode. The film was identified as the polymer having the following structure:



Example 12: Electrochemical polymerization of pyrrole disulfide 15

Pyrrole disulfide 15 synthesized according to Example 4 was polymerized electrochemically and its electrochemical properties were determined in a similar manner to Example 11. The peak potentials of oxidation and reduction were respectively 813 mV and 661 mV.

Example 13: Electrochemical polymerization of pyrrole disulfide 22B

Pyrrole disulfide 22B synthesized in accordance with Example 6 was electrochemically polymerized and determined with respect to electrochemical properties in a similar manner to Example 11, except for that propylene carbonate containing 0.5 M LiClO₄ was used as the electrolyte.

The peak potentials for oxidation and reduction were respectively 790 mV and 574 mV.

Claims:

1. A sulfur-containing compound represented by the following formula (I):

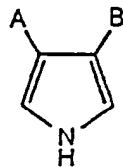


wherein Y represents NH or S; A represents hydrogen, a halogen atom or $-(CH_2)_m-SR^1$; and B represents $-(CH_2)_n-SR^2$, $-R^3-(S)_p-R^4-\text{cycloalkyl}$, $-R^5-SR^6$, $-(S)_q-\text{cycloalkyl}$ or $-SR^7$,

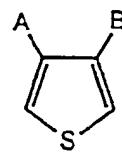
where R^1 , R^2 , R^6 and R^7 each represent hydrogen, an alkyl group, an alkyl-carbonyl group or an aryl group; R^3 , R^4 and R^5 each represent an alkylene group or an arylene group; m and n each independently represent an integer of 0, 1, 2 or 3, provided that m and n are not 0 simultaneously; p and q each independently represent an integer of 0, 1 or 2 and Y represents NH or S; and A and B may be combined to form $-(CH_2)_m-S-S-(CH_2)_n-$.

2. The sulfur containing compound according to Claim 1, wherein the compound is represented by the following formula [1] or [2]:

[1]



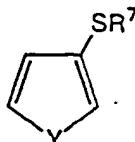
[2]



wherein A and B each have the same meanings as defined in Claim 1.

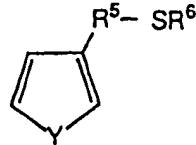
3. The sulfur containing compound according to Claim 2, wherein the compound is a compound selected from the group consisting of the following formulae [3] - [9]:

[3]



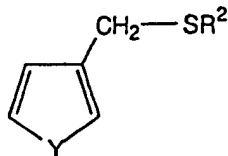
wherein R⁷ represents a hydrogen atom, an alkyl group or an aryl group; and Y represents an imino group or a sulfur atom;

[4]



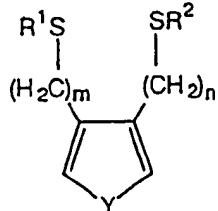
wherein R⁵ represents an alkylene group or an arylene group; R⁶ represents a hydrogen atom, an alkyl group or an aryl group; and Y represents an imino group or a sulfur atom;

[5]



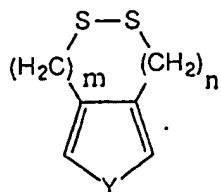
wherein Y represents an imino group or a sulfur atom; and R² represents a hydrogen atom, an alkyl group or an aryl group;

[6]



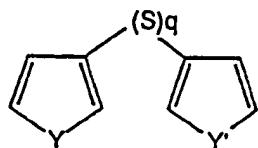
wherein Y represents an imino group or a sulfur atom; R¹ and R² each represent a hydrogen atom, an alkyl group, an alkylcarbonyl group or an aryl group; and m and n each represent an integer of 0, 1, 2 or 3 provided that m and n are not 0, simultaneously;

[7]



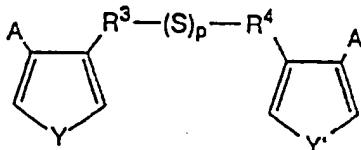
wherein Y represents an imino group or a sulfur atom; and m and n each represent an integer of 0, 1, 2 or 3 provided that m and n are not 0, simultaneously;

[8]



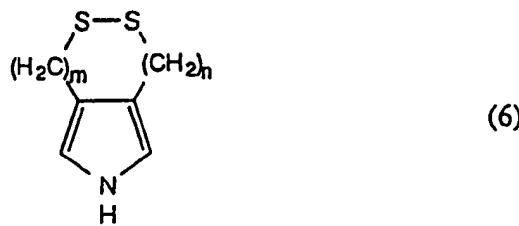
wherein Y and Y' each represent an imino group or a sulfur atom; and q represents an integer of 1 or 2; and

[9]



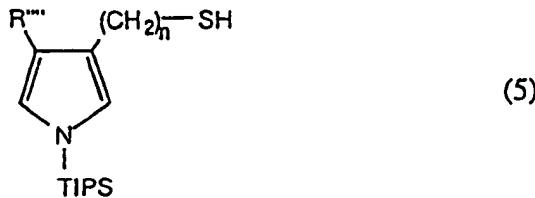
wherein A represents hydrogen or a halogen atom; Y and Y' each represent an imino group or a sulfur atom; R³ and R⁴ each represent an alkylene group or an arylene group; and p represents an integer of 1 or 2.

4. The sulfur containing compound according to Claim 3 wherein R¹, R², R⁶ and R⁷ each represent an alkyl group having 1 to 6 carbon atoms, an alkylcarbonyl group having 1 to 6 carbon atoms, a phenyl or naphthyl group; and R³, R⁴ and R⁵ each represent an alkylene group having 1 to 6 carbon atoms, a phenylene group or a naphthylene group.
5. The sulfur containing compound according to Claim 3 wherein R¹, R², R⁶ and R⁷ each represent an alkyl group having 1 to 3 carbon atoms, an alkylcarbonyl group having 1 to 3 carbon atoms, or a phenyl group; and R³, R⁴ and R⁵ each represent a methylene, ethylene or propylene group.
6. The sulfur containing compound according to Claim 3 wherein R¹, R², R⁶ and R⁷ each represent ethyl, acetyl or phenyl; and R³, R⁴ and R⁵ each represent methylene.
7. A method for preparation of the compound represented by the following formula (6):



wherein m and n each represent an integer of 0, 1, 2 or 3, provided that m and n are not 0, simultaneously,

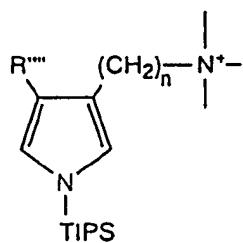
which comprises converting a thiol intermediate represented by the following formula (5):



wherein TIPS is triisopropylsilyl; R''' represents $-(CH_2)_m-SH$; and m and n have the same meanings as defined above, to the objective compound (6).

8. The method according to Claim 7, wherein the reaction is conducted at a temperature below 0 °C in an organic solvent.

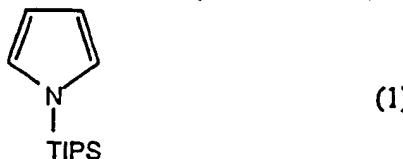
9. The method according to Claim 7, wherein said thiol intermediate is obtained from a pyrrole salt represented by the formula:



wherein TIPS is triisopropylsilyl; R''' represents $-(CH_2)_m-N^+-$; and m and n each represent an integer of 0, 1, 2 or 3, provided that m and n are not 0, simultaneously.

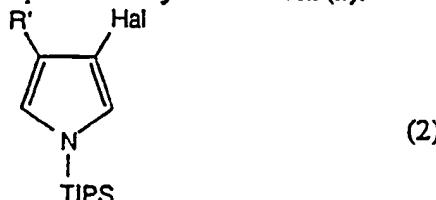
10. The method according to Claim 7, wherein the thiol intermediate of the formula (5) is obtained by the steps of:

(a) halogenating a compound represented by the formula (1):



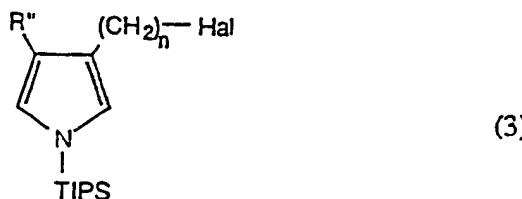
wherein TIPS is triisopropylsilyl,

to obtain an intermediate represented by the formula (2):



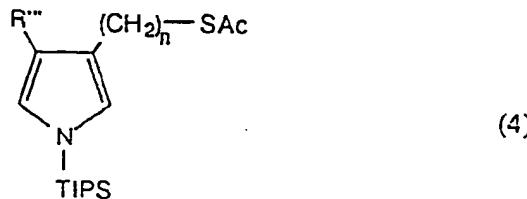
wherein R' represents a halogen atom, Hal represents a halogen atom and TIPS has the same meaning as defined above,

(b) followed by lithiating and alkylating the intermediate (2) to obtain a halogenated intermediate represented by the formula (3):



wherein R'' represents a halogen atom or -(CH₂)_m-Hal; m and n each represent an integer of 0, 1, 2 or 3 provided that m and n are not 0, simultaneously; and Hal and TIPS have the same meanings as defined above,

(c) then converting the halogenated intermediate (3) to a thioester represented by the formula (4):



wherein R''' represents a halogen atom or -(CH₂)_m-SAC; Ac is acetyl; and m, n, Hal and TIPS have the same meanings as defined above,

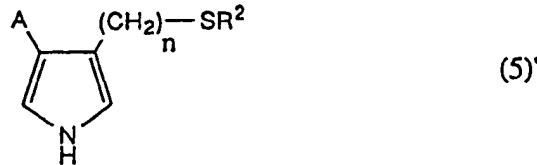
(d) and finally followed by reducing the thioester (4) to form the thiol intermediate represented by the formula (5).

11. The method according to Claim 9, wherein the reaction step (a) is conducted in a

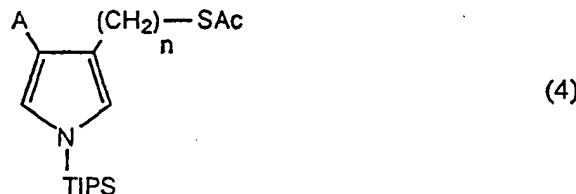
dichloromethane solvent.

12. The method according to Claim 9, wherein the reaction step (c) is conducted in the presence of potassium thioacetate.

13. A method for preparation of the compound represented by the following formula (5):



wherein A represents hydrogen or $-(CH_2)_m-SR^1$; R^1 and R^2 each represent a hydrogen atom, an alkyl group or an aryl group; and m and n each represent an integer of 0, 1, 2 or 3 provided that m and n are not 0, simultaneously, which comprises reducing and deprotecting a thioester compound represented by the following formula (4):



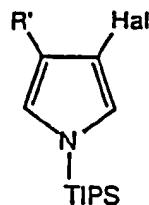
wherein A has the same meaning as defined above; Ac is acetyl; TIPS is triisopropylsilyl; and n has the same meaning as defined above.

14. The method according to Claim 12, wherein the thioester (4) is obtained by the steps of:

(a) halogenating a starting compound represented by the following formula (1):



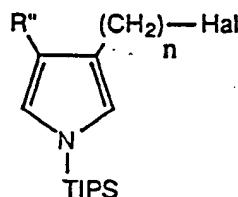
wherein TIPS is triisopropylsilyl, to obtain an intermediate represented by the following formula (2):



(2)

where R' represents hydrogen or a halogen atom; Hal represents a halogen atom; and TIPS has the same meaning as defined above,

(b) followed by lithiating and, if necessary, alkylating the intermediate (2) to obtain a halogenated intermediate represented by the following formula (3):

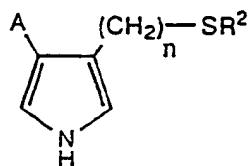


(3)

wherein R'' represents hydrogen or -(CH2)n-halogen; Hal and TIPS have the same meaning as defined above; and n represents an integer of 0, 1, 2 or 3.

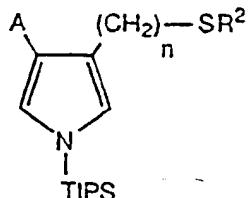
(c) and finally followed by converting the halogenated intermediate (3) to the thioester (4).

15. A method for preparation of the compound represented by the following formula:



wherein A represents hydrogen or -(CH2)m-SR¹; and R¹ and R² each represent a hydrogen atom, an alkyl group or an aryl group,

which comprises deprotecting a thiol intermediate represented by the following formula (6)':



(6)'

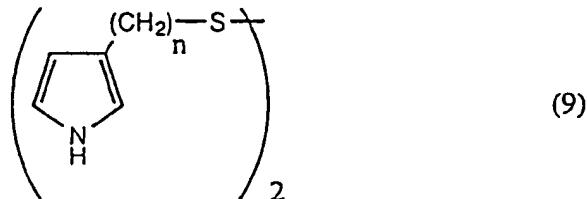
wherein A and R² have the same meaning as above; and TIPS is triisopropylsilyl.

16. The method according to Claim 14, wherein the thiol intermediate (6)' is obtained by reducing a thioester intermediate represented by the following formula (4):

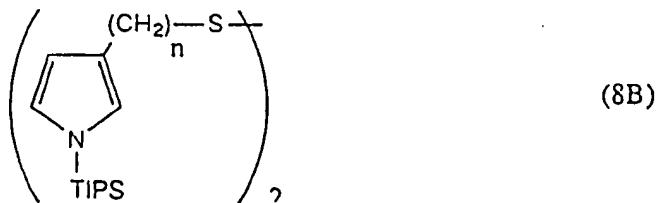
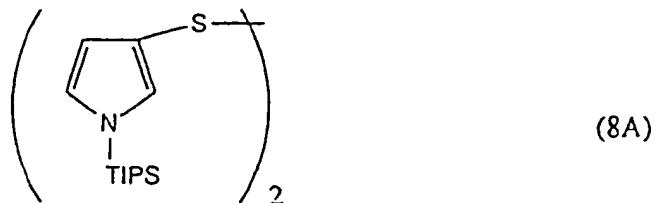


wherein A represents hydrogen or -(CH₂)_m-SR¹; R¹ represents a hydrogen atom, an alkyl group or an aryl group; Ac is acetyl; and TIPS is triisopropylsilyl.

17. A method for preparation of the compound represented by the following formula (9):



wherein n represents an integer of 0, 1, 2 or 3, which comprises deprotecting a disulfide compound represented by the following formula (8A) or (8B):



wherein TIPS is triisopropylsilyl; and n represents an integer of 1, 2 or 3.

18. The method according to Claim 16, wherein the disulfide (8A) or (8B) is obtained by the steps of:

(a) halogenating a compound represented by the following formula (1):



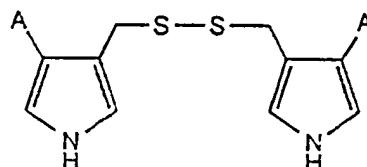
wherein TIPS is triisopropylsilyl,
to obtain an intermediate represented by the following formula (7):



wherein Hal represents a halogen atom, and TIPS has the same meaning as defined above,

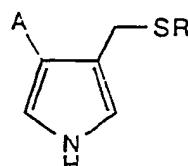
(b) and lithiating the intermediate (7), followed by reaction with sulfur to obtain the disulfide (8A), or by alkylation, reaction with NaSH, and conversion to the disulfide (8B).

19. A method for preparation of the compound represented by the following formula:



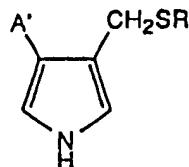
wherein A represents a hydrogen atom, a halogen atom or $-(CH_2)_m-SR^1$ where R^1 represents a hydrogen atom, an alkyl group or an aryl group; and m represents an integer of 0, 1, 2 or 3,

characterized by using Ellmann's reagent to convert a thiol intermediate represented by the following formula:



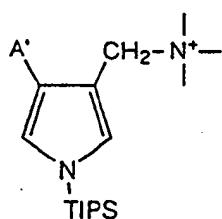
wherein R represents a hydrogen atom, an alkyl group or an aryl group, to the objective compound.

20. A method for preparation of the compound represented by the following formula :



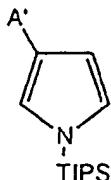
wherein A' represents a hydrogen atom, SR¹ or -(CH₂)_m-SR² where R¹ represents a hydrogen atom, an alkyl group or an aryl group, R² represents an alkyl group or an aryl group and m represents an integer of 1, 2 or 3; and R represents a hydrogen atom, an alkyl group or an aryl group.

which comprises converting an intermediate represented by the following formula:



wherein A' has the same meaning as defined above; and TIPS is triisopropylsilyl.

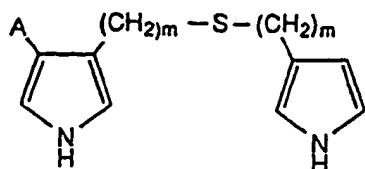
21. The method according to Claim 19, wherein the intermediate is obtained by converting a compound represented by the following formula:



wherein A', R¹, R², m and TIPS have the same meanings as defined in Claim 19,

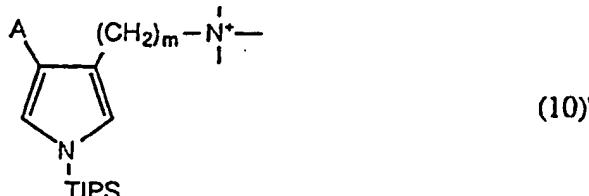
in the presence of Eschenmoser's salt.

22. A method for preparation of the compound represented by the following formula:



wherein A represents a hydrogen atom, a halogen atom or $-(CH_2)_m-SR^1$, and m and n each represent an integer of 1, 2 or 3 provided that m and n are not 0, simultaneously,

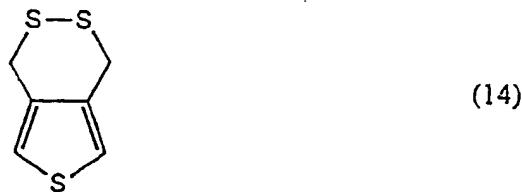
which comprises converting an intermediate represented by the following formula (10)':



wherein A and m have the same meanings as defined above, and TIPS is triisopropylsilyl.

in the presence of an alkali metal sulfide to the objective compound.

23. A method for preparation of the compound represented by the following formula (14):



which comprises converting a compound represented by the following formula (13):



wherein Z represents an alkali metal,
to the objective compound (14).

24. The method according to Claim 22, wherein the compound (13) is obtained by the steps of:

(a) halogenating a starting compound represented by the following formula (10):

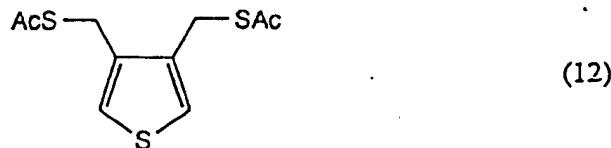


in the presence of azobisisobutyronitrile to obtain a compound represented by the following formula (11):



wherein Hal represents a halogen atom,

(b) converting the compound (11) to a thiol ester represented by the following formula (12):



wherein Ac represents an acetyl group,

(c) and then converting the thiol ester (12) to the compound (13) in the presence of an alkali metal thioacetate represented by the following formula:



wherein Z represents an alkali metal; and Ac has the same meaning as defined above.

25. The method according to Claim 22, wherein the compound (13) is converted to the objective compound (14) in the presence of Ellman's reagent.

26. An electroconductive polymer prepared by polymerization of the compound represented by the formula (I) according to Claim 1.

27. A method for preparation of electroconductive polymers starting from the monomers according to Claim 1, wherein said polymers are prepared by polymerization of the compound represented by the formula (I), or optional mixtures thereof, provided

that R¹, R^{1'}, R², R³, R⁴, R⁵, R⁶ and R⁷ are not aryl.

28. The method according to Claim 26, wherein the polymerization is an electrochemical polymerization.

29. The method according to Claim 27, wherein the electrochemical polymerization is conducted in an organic solvent in the presence of an alkali metal perchlorate.

30. The method according to Claim 27, wherein the electrochemical polymerization is conducted at a current density of 0.5 - 20 mA/cm².

31. The method according to Claim 26, wherein the polymerization is a chemical polymerization.

32. Use of the electroconductive polymer according to Claim 25 for the manufacture of an electrode active substance for battery.

Relevant Technical Fields	Search Examiner P N DAVEY
(i) UK Cl (Ed.M) C2C (CQQ, C2F)	Date of completion of Search 2 JUNE 1994
(ii) Int Cl (Ed.5) C07D 207/30, 333/04	Documents considered relevant following a search in respect of Claims :- 1-32
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASES: CAS ONLINE	

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Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.	E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
A: Document indicating technological background and/or state of the art.	&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X	Synth, Met., 40(3), 299-307	1 at least
X	J Chem Soc., Perkin Trans 2(5), 699-704	1 at least
X	J Org Chem., 52(24), 5382-6	1 at least
X	J Org Chem., 49(11), 2025-7	1 at least
X	An Quim., Ser C, 77(2), 105-11	1 at least

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